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砂発明の名称 硬表面の洗浄方法

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1. 発用の名称

優製面の気が方法

2. 特許課求の範囲

有機系員物が存在する軽点面を依存数により洗 かした後に性性する状形方法において、前記状序 並による洗浄の任意の工程の前に前記硬表面に無 外数を図引する工程を設けたことを特徴とする硬 裏面の水形方法。

1. 発明の詳細な説明

【農衆上の利用分野】

本几明は役害面の洗浄方法に係り、詳しくは、 例えば半導体プロセスにおいてフォトマスクブランクやフェトマスク、あるいは半線体基板等を洗 かずる君台に用いられる歴式洗浄方法に関する。 (世春の珍媛)

世来この所の遊式状形方法としては、一般に、 被状形物を少なくとも2種以上の失序被(例えば 観想、純水、アルコール等)に取次説数し、必要 に応じて状形披中に超額数を伝鞭させて状形処理 した頃、アルコール等の最気により肌が疲を気化 し代表する方法が知られている。

【預明が保收しようとする問題点】

しかしながら、上記した歴式気疹方法により彼 旅り包を洗浄処理した場合、 洗浄処理したにもあ らず、旅作処理機の施族が物に行れの存在が益め られる。その「原因として、雑枝を物上に囚むして いる残骸レグスト等の有機系異物が上記洗剤処理 によって充金には散去されずに洗が処理後も被抗 伊物上に一部残留することが挙げられる。 また住 の気因として、被抗を物上に囚犯している投出レ ツスト等の存職系具物が氏序処理に用いられる点 協設等の技計器と化学反応して独決が物の表面に 新たな反応を収集として比較することが無けられ る。さらにもう1つの原因として、先か処理にお いて用いられる異なる健康の抗療症の化学反応に より、被洗浄物の表面に新たな反応生成物が生じ ることが挙げられる。この異なる種類の先子披肩 心の七手反応による行れの死生について更になり 的に述べると、この種の独洗が他の洗が処理には、

上述の如く従来のおば洗浄方法では、被洗浄物の表面に図をしている有機系典物がらなる時代を元全に除去することは図数であり、この有機系典物と洗浄をとの反応、洗浄機商志の反応により新たな時代が被洗浄物の表面に発生するという問題点があった。

物が残留することがない。

また常外の昭朝処理によって前記の有機系具物は状序線による秩序処理時に被抗序物の表面上に最早存在していないので、有機系具物と秩序をとの化学反応により折たな反応生成物が被洗序物流面上に形成状務することもない。

【食品剂】

本党前は、ここような関節点を解決するためになされたものであり、その目的は、被洗浄物の表質に囚打した打理系質物からなる所れを完全に改生し取ると共に洗浄地理に作う折たな時れの発生のない飲み方法を最低することにある。

【問題点を解決するための手段】

本見明は、上記目的を達成させるためになされたものであり、有機展開物が存在する観音面を洗浄をより洗浄した後に乾燥する洗浄方法において、前記洗浄液による洗浄の任意の工程の自に前記を表面に無外数を取引する工程を設けたことをも色のである。

[金币]

洗浄銀による洗浄前に被洗浄物に食外数を削引することにより、被洗浄物の表面に残倒しているフェトレジスト等の有間系具物が化学を化を受け、その根で分解質失したり、その根の洗浄数による洗浄処理において洗浄数によって溶解又は影解しやすい状態になるので、被洗浄物の洗浄技による洗浄処理技に放洗浄物の表面上に前記の有数系具

被状形物の収度秩序、純水状形及びイソプロピルアルコール(以下【PAと昭称する)状態を設 次行なった糖、被洗浄物を【PA証例を用いて化 費する従来のフォトマスク状形方法において、被 競技市前に被洗浄物を無外線照射処理する支油例 について以下に製削する。

被比が物として、周知のレジストエ記、エッチングエ母のよびフォトレジスト制能工程を登れたのは、たったで、放け作物であるフォトマスクは、透光性パラス基板上にクロム基光性機を被引してなるフォトマスクテンク上にポジタフォトレジストである人で、カンを介して対比、現象した後、レジストパターンを可以したものである。

このフォトマスク(大きさ5×5×0,09インチ)4枚を、低圧水銀灯を異視してなる意外粒型別質器(処理室容額:3240m³)内に配置

し、素外数原列心理を行なった。

弘元条件は、以下の送りである。

男外の位… 2537人の耳中の包皮が全体の 90%、1849人の舞蹈の強度が 今はの数%である低圧水型灯を用い

低圧水型灯に供給する数パワーー 7 7 0 W . ウェットエアー…常外自反射装置のガス導入口 から301/分の装造で導入した。 ウェットエアーは紫外線機関質に 03 の発生効率を向上させる作用を

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女外袋煎引動を後の並洗を物を次いで洗浄料理 し、松煌処理した。すなわち、抗彦処理は、被抗 かわを確立98%の回貨銀1指に5分間長頭し、 次に美水1倍に30分間提及し、型に「PA1倍 に3分回提思することにより行なった。なり筆 **抗市物のIPA権投資に際しては、IPA腋中に** 出品数(45kHz と46kHz の周数数を交互に載 り乗し見生する発音器を使用した。パワーは40 OWである。) を伝戴して四日放光がを行なった。 幕配 抗炸処理協の技量処理は「PA給から引 を上げられた世氏が数を1PA意気には許するこ とにより行なった。

上記の仰く葉外腺照射処理機に洗浄、乾燥処理 された雑誌伊物16枚について、その城市化の位 合を担償したが、18枚ともに方れが思められな かった.

なお、素外線型引動配を行なわずに同様の状態。 松桑処理を行なった被洗浄物15枚についても剪 はにその爪声をの収合を収収したが、15枚とも に全面に汚れが思められた。また灰が処理におい て美水便数後移動理を3階とし、各槽投資期間を それぞれ100岁としても、無外数を虹別しない 着合には触洗浄物の全面に汚れが深められること

この支持側の結束から、無外数規制処理を行む う本発明の方法によれば、被洗浄物表面上に固む している有国系集物が効果的に放去されており、

かつ状形的現時の化学反応に伴う新たな反応生成 もの丘生もないので、抗浄虹症後の破疾が動の環 かせが十分に異なされることが明らかである。

上の変換的では各族が物として、ボジ型(光分 解型)フォトレジストが収留囚着しているフォト マスクを用いたが、本発明の方法においてはネガ 型(光硬化型)フォトレジストが残骸回着してい る旅院作物を洗浄処理するこもでき、またレジス トがポジ型及びネガ型電子器レジストであっても

また本苑明の方近は、フォトマスクの洗浄に豊 足されるものではなく、フォトマスクプランク、 ・ガラスは収、武引導電視行きガラス基板、シリコ ンウェハ等、更にほカメラレンズ等の光学レンズ や取扱レンズを被抗が物とし、これらの表面に付 巻乃至囚告している有機系異物(例えば大気中の こみに山来する汚染物や手根搭触による月染物等) を重好することが知せしい。 を放去するためにも用いられる。

また紫外韓国朝条件は、雑鉄浄物の材質及び鉄 市場理論に経てきた工程等により重宜選定しうる。 景外韓国製処理時期はこれに担定されるものでは

すなわち、常外和を照明する先輩として、水田ア - クランプ、中圧水量ランプ、高圧水塩ランプ、 キセノンランプ、低水ランプ界も用いてもよく、 また導入ガスとして、上の支援質で用いたウェッ トエアーの代りにドライエアーヤオソン(〇、) 等を使用しても良く、さらにパワー、処理時間を も任意に変勢させることができる。また起来なの ガスを含有する雰囲気中で常外値を放射しても良 く、この場合には開業が無外線質的時にオゾンに なって、被抗が物上に付着している汚れ成分の酸 **化分解等が促進される。またアルゴン、窓裏での** 不抵性ガスを含有する雰囲気中で意外線を取引し ても良い。取割する衆外腺の放及は上の支援例に 記したもの以外に任意の独臣であってよいが、有 **複数での発生を効果的に減少・粒去せしめるため**

また上の支施例では、緩破洗浄に先立って案外 雑型別処理を行なったが、本見市の方法において、 なく、製造化が後で発水状作的または低水及が低で 1 PA 洗が的に無外線照射処理を実施しても良く、また例えば発療状が前及び破離状が微で循水 状形的の組く無外線照射処理を 2 個以上行なって も良い。

また上の支援的では、無外的取別が思想での洗浄 処理として、情報、特水、1P人において用いたり 地元を区別したが、本見引の方法においてはいら れるは単値によれて配定されるものではない があるにはかまれのみ、1P人のみ、またになる 他化水果と1P人を向いる液浄処理を採用すると とがそのいる洗浄処理をはは、水のみまたは「P人 とがそのいる洗浄処理においな次浄他の または「P人による洗浄的化水素水洗浄値の または「P人による洗浄的化水素水洗浄値の を使が行なわれ、また透性化水素水洗浄値、透透にり る洗浄処理では、洗浄的または純水洗浄値でな 条水洗浄的の任意の 及物に無外数配割返避が行い とのために

もちろん被抗をもの抗療技中への浸漉洗みに際

スク、フォトマスクプランク、ガラス基板、半導[・] 体は低等、更には光学レンズや難算レンズ等の硬

表面を有する物品を効果的に関ひむすることを実現するものであり、その工業的産業は極めて多大である。

特許出職人 本一 7 株 式 会 社 代理人 非理士 中 4 都 男 して、共序級中におお譲せ伝習させたり、あるい 以他技術者を延載させたりすることは任立てある。

また乳の物理として、上述の被肌の物を肌の変中に設置する方法の代りにスピンナー等で被肌が 物を回転させながら洗剤後をスプレーする方法や 雑洗の物に加圧(百圧ジェット化)された洗剤機 を助きつける方法などを拡加することもできる。

上の実施例では最後かちの乾燥を埋として、 I P A 磁気による超低を増発を採用したが、フロンギの他の温気を用いる温気を増でも良く、またスピン乾燥でも良い。

本見切の方はは、常外範型的処理を行なわない 適常の氏わ方性を実施した結果、異なる形質の洗 沙臓(何えば磁能とアルコール)の化学反応によ る時れが発生した進光砂能の可洗浄のためにも有 熱であり、展外範型射処理機に洗浄酸による所決 浄処理を行なうことによって、適常の条件では除 去個質な汚れを除去することが可能である。

[元明の効果]

以上非難したように、木朮切の方法はフェトマ

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SPECIFICATION

1. Title of the Invention: METHOD FOR CLEANING HARD SURFACE

2. Claim

A method for cleaning a hard surface having organic foreign substances, comprising cleaning the hard surface with a cleaning solution, followed by drying, wherein a step of irradiating the hard surface with ultraviolet light is provided before any given step of cleaning with the cleaning solution.

Detailed Description of the Invention
 [Industrial Field of the Invention]

The present invention relates to a method for cleaning a hard surface, and more particularly relates to a wet cleaning method which is used, for example, when a photomask blank, a photomask, a semiconductor substrate, or the like

is cl aned in a semiconductor process.

[Description of the Related Art]

The known wet cleaning method generally includes the steps of cleaning by immersing a workpiece to be cleaned in at least two cleaning solutions (e.g., sulfuric acid, pure water, and alcohol) one after another, and as required, by propagating ultrasonic waves into the cleaning solutions, and then drying by vaporizing the cleaning solutions by means of vapors of alcohol or the like.

[Problems to be Solved by the Invention].

However, when a workpiece is subjected to cleaning treatment by the wet cleaning method described above, the workpiece after cleaning is observed to have contamination in spite of the cleaning treatment. One of the reasons for this is that organic foreign substances such as a residual resist stuck on the workpiece are not completely removed by the cleaning treatment and partially remain on the workpiece after the cleaning treatment. Another reason is that organic foreign substances such as a residual resist stuck on the workpiece chemically react with a cleaning solution such as concentrated sulfuric acid, and a new reaction product is deposited on the surface of the workpiece. Still another reason is that different types of cleaning solutions used in the cleaning treatment chemically react with each other, and a new reaction product is generated on the

surface of the workpiece. The g neration of contamination due to th chemical reaction between the different types of cleaning solutions will be further described in d tail. In order to clean this type of workpiece, for example, cleaning treatment in which concentrated sulfuric acid immersion cleaning and alcohol immersion cleaning are combined is employed. In this cleaning treatment, after concentrated sulfuric acid immersion cleaning is performed in one vessel, pure water immersion cleaning is performed in three vessels b fore alcohol immersion cleaning in one vessel. Even if such pure water cleaning treatment is intervened, when foreign substances or the like exist on the surface of the workpiece or surface wettability of the workpiece is not uniform, sulfuric acid sticks and remains on the surface of the workpiece after pure water treatment and reacts with alcohol in the subsequent alcohol immersion cleaning. treatment to generate a kind of esterified reaction product. In such a case, it is difficult to remove contamination due to the reaction product even by cleaning again with a cleaning solution such as sulfuric acid or alcohol, which is particularly troublesome.

As described above, in the known wet cleaning method, it is difficult to completely remove contamination due to organic foreign substances stuck on the workpiece, and new contamination may occur on the surface of the workpiece

because f a reaction between the organic foreign substances and a claning solution or a reaction between the individual claning solutions.

The present invention overcomes the foregoing problems. It is an object of the present invention to provide a method for cleaning in which contamination due to organic foreign substances stuck on the surface of a workpiece can be completely removed and new contamination associated with cleaning treatment can be prevented.

[Means for Solving the Problems]

The present invention was made to achieve the object described above, and in a method for cleaning a hard surface having organic foreign substances with a cleaning solution, followed by drying, a step of irradiating the hard surface with ultraviolet light is provided before any given step of cleaning with the cleaning solution.

[Operation]

By irradiating a workpiece with ultraviolet light before cleaning with a cleaning solution, organic foreign substances such as a photoresist that remain on the surface of the workpiece are subjected to a chemical reaction, and the organic foreign substances may be decomposed and disappear at that stage or may become to be easily dissolved or removed by a cleaning solution in the subsequent cleaning treatment with the cleaning solution. Therefore, the

organic f reign substances do not remain on the surface of the workpi ce after the cleaning treatment with the cleaning soluti n.

Additionally, by the ultraviolet radiation treatment, since the organic foreign substances do not exist on the surface of the workpiece any more during cleaning treatment, a new reaction product is not generated due to a chemical reaction between the organic foreign substances and the cleaning solution.

Moreover, since surface wettability of the workpiece is improved by the ultraviolet radiation treatment, the cleaning solution spreads over the surface of the workpiece uniformly, and cleaning treatment with the cleaning solution can be performed uniformly over the entire workpiece, and also draining is easily performed when the workpiece is withdrawn from the cleaning solution and the cleaning solution does not remain partially concentrated on a portion of the surface of the workpiece. Thereby, for example, in a cleaning method in which sulfuric acid immersion cleaning treatment and alcohol immersion cleaning treatment are combined, if a simple pure water immersion cleaning treatment step for eliminating sulfuric acid that remains slightly on the surface of the workpiece is provided between the sulfuric acid treatment and the alcohol treatment, new contamination due to a chemical reaction between sulfuric

acid and alcohol do s not occur.

[Example]

With resp ct to a conventional m thod for cleaning a photomask in which a workpiece is subjected to sulfuric acid cleaning, pure water cleaning, and isopropyl alcohol (hereinafter abbreviated as IPA) cleaning in that order, followed by drying using IPA vapors, an example in which the workpiece is subjected to ultraviolet radiation treatment before sulfuric acid cleaning will be described below.

As a workpiece, a photomask obtained by the known steps of resist, etching, and photoresist stripping was used.

That is, in order to obtain the photomask as a workpiece,

AZ-1350 (manufactured by Hoechst) as a positive photoresist was applied on a photomask blank in which a chrome shading film was formed on a transparent glass substrate, exposure and development were performed through a mask having-a predetermined pattern, the shading film was etched using the resist pattern as a mask, and then the resist pattern was stripped.

Four sheets of such a photomask with dimensions of 5 \times 5 \times 0.09 inch were placed in an ultraviolet irradiation system (treatment-chamber volume: 3,240 cm³) and ultraviolet radiation treatment was performed.

Treating conditions are as follows.

Ultraviolet source: low-pressure mercury-vapor lamp,

in which the intensity of an emission line at 2,537 Å occupies 90% and the intensity of an emission line at 1,849 Å occupies several percents of the total intensity.

Total power applied to low-pressure mercury-vapor lamp: 770 W

Wet air: Introduced at a velocity of 30 l/minute from a gas inlet of the ultraviolet irradiation system.

Wet air improves the efficiency of O₃ generation during ultraviolet radiation.

Treating time: 5 minutes

After ultraviolet radiation treatment, the workpiece was subjected to cleaning treatment, followed by drying treatment. That is, cleaning treatment was performed by immersing the workpiece in one-vessel concentrated sulfuric acid having a concentration of 98% for 5 minutes, next by immersing in one-vessel pure water for 30 seconds, and further by immersing in one-vessel IPA for 3 minutes. With respect to the immersion of the workpiece in the IPA vessel, ultrasonic cleaning was performed by propagating ultrasonic waves into the IPA solution. (An ultrasonic oscillator for generating frequencies of 45 kHz and 46 kHz alternately was used. Applied power was 400 W.)

Drying treatment after the cleaning treatment was performed by exposing the workpiece withdrawn from the IPA

v ss l to IPA vapors.

With r spect to 16 workpiec s which w re cleaned and dried aft r ultraviolet radiation treatment as described above, the cleanliness level was inspected. Contamination was not observed in all 16 workpieces.

With respect to 15 workpieces which were cleaned and dried in a similar manner without performing ultraviolet radiation treatment, the cleanliness level was inspected. Contamination was observed in the entire surfaces of all 15 workpieces. Even when pure water immersion cleaning treatment was performed in three vessels and the immersion time was set for 100 seconds each, contamination was often observed in the entire surface of the workpiece when ultraviolet radiation was not performed.

As a result of this example, in the method in which ultraviolet radiation treatment is performed in accordance with the present invention, organic foreign substances stuck on the workpieces are effectively removed and a new reaction product associated with a chemical reaction during cleaning treatment is not generated, and thereby it is clear that cleanliness of the workpieces after cleaning treatment can be secured satisfactorily.

Although in the example described above, a photomask stuck with a residual positive (photodegradable) photoresist was used, in the method in accordance with the present

invention, a workpi c stuck with a residual negative (photo-setting) photoresist may be cl aned, and in the case of positiv and negative electron beam resists, the method also can be used similarly.

The method in accordance with the present invention is not limited to cleaning of photomasks. Photomask blanks, glass substrates, glass substrates provided with transparent conductive films, silicon wafers, and the like, and additionally, optical lenses such as camera lenses and spectacle lenses may be considered as workpieces, and the method is used to remove organic foreign substances (e.g., contaminants due to dust in air or contaminants due to finger contact) attached or stuck to the surfaces thereof.

Ultraviolet radiation conditions may be selected appropriately depending on materials of workpieces and processes undergone before cleaning treatment. That is, as a light source for ultraviolet radiation, a mercury arc lamp, a medium-pressure mercury lamp, a high-pressure mercury lamp, a xenon lamp, a heavy-water lamp, or the like may be used. As an induction gas, instead of wet air used in the example described above, dry air, ozone (O₃), or the like may be used. Moreover, power and treating time may be varied voluntarily. Ultraviolet radiation may be performed in an atmosphere containing a gas such as oxygen, and in such a case, oxygen changes into ozone during ultraviolet radiation

and oxidative d struction or the like of contaminants stuck on the w rkpiece is accelerated. Ultraviolet radiati n may also be performed in an atmosphere containing an inert gas such as argon or nitrogen. Although ultraviolet light radiated may have a given wavelength in addition to that described in the example, in order to effectively reduce and remove foreign substances such as organic substances, it is desirable that ultraviolet light having a wavelength of 1,000 to 3,000 Å be radiated.

Although ultraviolet radiation treatment was performed before sulfuric acid cleaning in the example described above, the timing of ultraviolet radiation treatment is not limited to this in accordance with the method of the present invention. Ultraviolet radiation treatment may be performed after sulfuric acid cleaning and before pure water cleaning or after pure water cleaning and before IPA cleaning, or ultraviolet radiation treatment may be performed at least twice, for example, before sulfuric acid cleaning, and after sulfuric acid cleaning and before pure water cleaning.

With respect to cleaning treatment after ultraviolet radiation treatment, although sulfuric acid, pure water, and IPA were used in that order in the example described above, cleaning treatment used in the method of the present invention is not limited to this. For example, cleaning treatment using aqueous hydrogen peroxide only, IPA only, or

hydrog n peroxid and IPA may be adopted. In cleaning treatment using aqueous hydrogen p roxide only or IPA only, ultraviolet radiation treatment is performed before cleaning with aqueous hydrogen peroxide or IPA, and in cleaning treatment using aqueous hydrogen peroxide and IPA, ultraviolet radiation treatment is performed at a given stage before aqueous hydrogen peroxide cleaning, after aqueous hydrogen peroxide cleaning and before pure water cleaning, or after pure water cleaning and before IPA cleaning.

Of course, when a workpiece is subjected to immersion cleaning in a cleaning solution, ultrasonic waves may be propagated into the cleaning solution, or the workpiece may be oscillated.

As cleaning treatment, instead of immersing a workpiece in a cleaning solution as described above, a method-of spraying a cleaning solution while a workpiece is rotated by a spinner or the like, or a method of spraying a workpiece with a pressurized (high-pressure jet) cleaning solution may be adopted.

With respect to drying treatment of the workpiece, although vapor drying by IPA vapors was adopted in the example described above, vapor drying using other vapors such as flon may be used, or spin drying may be used.

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The method of the present invention is also effective

in r cl aning a workpi ce in which contamination has occurred due to a chemical reaction betw n diff r nt types of cleaning solutions (for xample, sulfuric acid and alcohol) as a result of carrying out a general cleaning process without ultraviolet radiation treatment. By recleaning treatment with a cleaning solution after ultraviolet radiation treatment, contamination that is not removable under normal conditions can be removed.

[Advantages]

As described above in detail, the method in accordance with the present invention makes it possible to effectively clean photomasks, photomask blanks, glass substrates, semiconductor substrates, and the like, and also articles having hard surfaces such as optical lenses and spectacle lenses, and the industrial significance of the invention is great.

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CLEANING OF HARD SURFACE

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ABSTRACT

PURPOSE: To prevent the occurrence of new contamination by a method wherein ultraviolet light is irradiated on the hard surface, whereon organic foreign substances exist, of a matter be cleansed before the matter to be cleansed is cleansed with a cleaning fluid.

CONSTITUTION: In case the hard surface, whereon organic foreign substances exist, of a matter to be cleansed is dried after being cleansed with a cleaning fluid, ultraviolet light is irradiated on the hard surface before the cleaning. That is, by irradiating the ultraviolet light on the matter to be cleansed before the matter to be cleansed is cleansed with the cleaning fluid, the organic foreign substances of a photo resist and so on remaining on the surface of the matter to be cleansed are subjected to chemical change, are decomposed and disappeared on the spot and are brought in a state that they are easy to dissolve or peel with the cleaning fluid in a cleaning treatment to be executed with a cleaning fluid subsequent to that. Thereby, it is eliminated that organic foreign substances remain on the surface of the matter to be cleansed after the matter to be cleansed is subjected to cleaning treatment with a cleaning fluid and the occurrence of new contamination can be prevented.